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FINAL REPORT

PUBLICATIONS/ PATENTS/ PRESENTATIONS/ HONORS/ STUDENTS REPORT

for

Contract N00014-91-J-1910

R&T Code 4131025

Title of Contract

"Aspects of Inorganic Electrochemistry"

Name(s) of Principal Investigator(s)

A.B.P. Lever

Name of Organization

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Part I

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(b) Papers Published in Refereed Journals

P. Seymour, Y.-H. Tse, N. Kobayashi, H. Lam, C.C. Leznoff and A.B.P. Lever, Surface Electrochemistry of Chloro(phthalocyanine)rhodium(III) Species, and Oxygen Reduction Electrocatalysis. Formation of a Dimeric Species. Inorg. Chem., 31, 4453-4459, 1991.

Y.-H. Tse, P.R. Auburn and A.B.P. Lever, The Trans-Cis Isomerisation of Bis(Dioxolene)bis(R-pyridine)Ruthenium Complexes. Can. J. Chem., 70, 1849-1854, 1992.

P.A. Bernstein and A.B.P. Lever, Protonation of Cobalt Tetraneopentoxyphtalocyanine as a Function of Oxidation State. Inorg. Chimica Acta, 198-200, 543-555, 1992.

N. Kobayashi, P. Janda and A.B.P. Lever, Cathodic Reduction of Oxygen and Hydrogen Peroxide at Cobalt and Iron Crowned Phthalocyanines Adsorbed on Highly Oriented Pyrolytic Graphite Electrodes. Inorg. Chem., 31, 5172-5177, 1992.

H. Masui, E.S. Dodsworth and A.B.P. Lever, Substituent Effects and Bonding Characteristics in o-Benzoquinonediiminebis(bipyridine) ruthenium(II) Complexes. Inorg. Chem., 32, 258-267, 1993.

A.B.P. Lever, Derivation of Metallophthalocyanine Redox Potentials via Hammett Parameter Analysis. Inorganica Chimica Acta, 203, 171-174, 1992.

H. Masui and A.B.P. Lever, Correlations Between the Ligand Electrochemical Parameter E(L) and the Hammett Substituent Parameter, σ . Inorg. Chem., 00, 0000, 1993.

Y.-H. Tse, A. Goel, M. Hu, C.C. Leznoff, J.E. Van Lier and A.B.P. Lever, Electrochemistry and Spectro-electrochemistry of Substituted Tetrabenzotriazaporphine. Can. J. Chem., 00, 0000, 1993.

(c) Technical Reports and Non-Refereed Papers

P. Seymour, Y.-H. Tse, N. Kobayashi, H. Lam, C.C. Leznoff and A.B.P. Lever, Surface Electrochemistry of Chloro(phthalocyanine)rhodium(III) Species, and Oxygen Reduction Electrocatalysis. Formation of a Dimeric Species. Inorg. Chem., 31, 4453-4459, 1991 (Technical Report #42).

Y.-H. Tse, P.R. Auburn and A.B.P. Lever, The Trans-Cis Isomerisation of Bis(Dioxolene)bis(R-pyridine)Ruthenium Complexes. Can. J. Chem., 70, 1849-1854, 1992 (Technical Report #43).

P.A. Bernstein and A.B.P. Lever, Protonation of Cobalt Tetraneopentoxypthalocyanine as a Function of Oxidation State. Inorg. Chimica Acta, 198-200, 543-555, 1992 (Technical Report #44).

N. Kobayashi, P. Janda and A.B.P. Lever, Cathodic Reduction of Oxygen and Hydrogen Peroxide at Cobalt and Iron Crowned Phthalocyanines Adsorbed on Highly Oriented Pyrolytic Graphite Electrodes. Inorg. Chem., 31, 5172-5177, 1992 (Technical Report #47).

H. Masui, E.S. Dodsworth and A.B.P. Lever, Substituent Effects and Bonding Characteristics in o-Benzoquinonediiminebis(bipyridine) ruthenium(II) Complexes. Inorg. Chem., 32, 258-267, 1993 (Technical Report #48).

A.B.P. Lever, Derivation of Metallophthalocyanine Redox Potentials via Hammett Parameter Analysis. Inorganica Chimica Acta, 203, 171-174, 1992 (Technical Report #49).

H. Masui and A.B.P. Lever, Correlations Between the Ligand Electrochemical Parameter E(L) and the Hammett Substituent Parameter, σ . Inorg. Chem., 00, 0000, 1993 (Technical Report #51).

Y.-H. Tse, A. Goel, M. Hu, C.C. Leznoff, J.E. Van Lier and A.B.P. Lever, Electrochemistry and Spectro-electrochemistry of Substituted Tetrabenzotriazaporphine. Can. J. Chem., 00, 0000, 1993 (Technical Report #52).

Non-Refereed Papers:

A.B.P. Lever, E.R. Milaeva and G. Speier, The Redox Chemistry of Metallophthalocyanines in Solution, The Phthalocyanines, Properties and Applications, Vol. 3 ed. C.C. Leznoff and A.B.P. Lever, VCH, New York, 1993 (Technical Report #45).

A.B.P. Lever, The Parameterisation of Metal Centred Redox Couples, Proceedings of NATO Advanced Research Workshop - Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds, Sintra (Portugal), March 25, 1992. Coord. Chem. Rev., 00, 0000, 1993 (Technical Report #46).

H. Masui, R. Metcalfe, D.J. Stufkens, E.S. Dodsworth, P.R. Auburn and A.B.P. Lever, The Ground and Excited State Electronic Structures of Ruthenium Quinones and Related Species, Coord. Chem. Rev., 00, 0000, 1993 (Technical Report #50).

(h) Number of Invited Presentations at Workshops or Professional Society Meetings

Invited Speaker, 5th Canadian Hydrogen Workshop, Ottawa, February 1992.

Invited Lecturer, NATO Advanced Research Workshop - Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds, Sintra (Portugal), March 1992.

Invited Lecturer, The Chemical Institute of Canada, Edmonton, June 1992.

Invited Lecturer, XXIX International Conference on Coordination Chemistry, Lausanne, Switzerland, July 1992.

Invited Lecturer, Perspectives in Photochemistry - International Symposium Honouring V. Carassiti, Ferrara, Italy, October 1992.

(1) Other funding

1989/90- Supply and Services Canada, Study for the Removal of Hydrogen
1991/92 Sulphide from Claus Process Effluent and the Recovery of
Economic Quantities of Sulphur and Hydrogen,
\$47,000, \$116,000, \$56,061.

1990/92 Supply and Services Canada, Feasibility Study for the Removal
of Hydrogen Sulphide, \$17,500.

1991/92- NSERC - Operating, Spectroscopic and Electrochemical Studies in
1993/94 Coordination Chemistry, \$52,000, \$52,000, \$52,000.

1992/93- Supply and Services Canada, Study of Switchable Plastics,
1993/94 \$118,055, \$86,995.

1992/93 NSERC - Strategic (with Pietro, Oldham), Phthalocyanine
Film Array Sensors, \$127,400.

Part II
LEVER/ONR

-4-

(a) Principal Investigator

A.B.P. Lever, York University, Chemistry Department

(b) Current Telephone Number

(416) 736-2100, Extension #22309

(c) Cognizant ONR Scientific Officer

R. Nowak

(d) Brief description of project.

Electrochemical studies are carried out in three main areas.

- i) Phthalocyanine electrochemistry: emphasis is placed on the chemistry of phthalocyanine modified electrodes for the study of electrocatalytic processes ultimately leading to chemical sensors. These studies include polymeric phthalocyanine conductive species. We also seek a comprehensive understanding of phthalocyanine electrochemistry to benefit all phthalocyanine redox applications. This work is extended to include Langmuir Blodgett (LB) surface (monolayer) phthalocyanine films with spectroelectrochemical studies being undertaken in situ on the trough surface.
- ii) Redox active ligands and electronic structure: A broad range of chemical techniques (uv/vis/FTIR/resonance Raman/PES/ X-ray/ Electrochemistry/solvatochromism/ ab initio calcs. are brought into play to understand the electronic structures, spectroscopy and electrochemistry of ruthenium (mainly) complexes of quinonoid ligands (including derivatives such as quinonediimines) where oxidation states are non-integral.
- iii) In situ LB Electrochemistry: Studies of the interactions of surface films with subphase redox species, in situ, in an LB trough. This is exploratory work aimed at developing methods for creating arrays of molecules and studying them through electronic spectra and electrochemistry - towards nanotechnology.

(e) Significant results.

A complete and novel study of the electronic spectroscopic characteristics of protonated cobalt phthalocyanines as a function of (four) different oxidation states (TR #44). Analysis of the surface behavior of rhodium phthalocyanine, as a modified electrode, demonstrating the ability to place either mononuclear or binuclear RhPc species on the surface as desired, and illustrating their (reversible) interconversion (TR #42). A comprehensive analysis of the solution electrochemistry of (all) metallophthalocyanines species, including predictive capability through Hammett plot analysis (TR #45). Extension of our newly introduced electrochemical parametrization of metal centred redox couples (TR #46). A study of the oxygen reduction

electrocatalysis by crown substituted Co and Fe phthalocyanines (TR #47). A very detailed analysis of the changes in electronic structure observed in E_2 -quinonediimine ruthenium species as a function of substituent R (TR #48). Further development of the interface between optical and electrochemical data (Vlcek/Dodsworth/Lever). Study of an unusually solvatochromic biphenyl ligand complex whose twist angle depends upon the presence of donor or acceptor solvents (Dodsworth/Metcalfe/Lever - submitted). Relationships developed between Hammett substituent constants and electrochemical parameters (TR #51). An introductory comparative study of the electrochemical and spectroscopic behaviour of phthalocyanines and triazabenzoporphyrins (TR#52). A study of the possible electronic coupling between ferrocene and phthalocyanine units in a tetraferrocenylphthalocyanine species (Lever/Leznoff/Tse/Li, in press, tech. rep. in preparation). The first major comprehensive review of the solution electrochemical behaviour of metallophthalocyanines has recently been published (TR#45).

(f) Brief summary of plans for next years work.

i) Phthalocyanine electrochemistry: The surface electrochemistry of phthalocyanine modified electrodes will be continued with emphasis on the chemistry of electropolymerized phthalocyanine conductive surfaces. This will include the use of ultramicroelectrode arrays where each ultramicroelectrode (ca 25 micron diameter) is a MPC modified surface (chemical sensors). In situ LB surface behavior and spectroelectrochemistry, with a view to constructing organized donor-acceptor complexes at the LB surface. Systemization of phthalocyanine redox potentials towards the ability to predict potentials for hitherto unprepared species.

ii) Redox active ligands: Extension of earlier studies to rhenium and osmium. Creation of bi- and polyfunctional redox systems (two (or more) redox centres linked by various length bridges) and their incorporation into LB films. Studies of electron transfer between organized redox centre arrays using spectroscopic and electrochemical techniques.

iii) Towards nanotechnology: Reactions of these polyfunctional redox films with subphase redox species and with redox centre modified electrodes. The creation of vectorially organized electron transfer pathways with both downhill and uphill components.

iv) Extension of the electrochemical parametrization concept to overlap Tolman electronic factors and other previously introduced parametrization schemes and especially to study organometallic sandwich complexes. Thus to move towards a global application of these electrochemical parameters for many applications.

- (g) List of names of graduate students and post-doctoral(s) working on the project.

PDFs - E.S. Dodsworth, J. Ouyang, W. Torres.

Graduate Students - Z. Jin, Y. Fu, Y.-H. Tse, H. Masui, A. Del Medico, P. Bernstein.

Consultant - H. Lam.